

WHAT IS CLAIMED IS:

1. A method for reducing catalyst attrition losses in hydrocarbon synthesis processes conducted in high agitation reaction systems, said method comprising the step of reacting a synthesis gas in a high agitation reaction system in the presence of a catalyst comprising a γ -alumina support, wherein said γ -alumina support includes an amount of titanium effective for increasing the attrition resistance of said catalyst in said high agitation reaction system.

2. The method of claim 1 wherein said titanium is present in said γ -alumina support in an amount of at least 800 parts per million by weight.

3. The method of claim 1 wherein said titanium is present in said γ -alumina support in an amount of at least 1000 ppm by weight.

4. The method of claim 1 wherein said titanium is present in said γ -alumina support in an amount in the range of from about 1000 to about 2000 parts per million by weight.

5. The method of claim 1 wherein said γ -alumina support has been produced from spray-dried, synthetic boehmite.

6. The method of claim 1 wherein said titanium is added to said γ -alumina support prior to the crystallization of said synthetic boehmite.

7. The method of claim 6 wherein said γ -alumina support has:
- a substantially spheroidal shape;
 - an average particle size in the range of from about 10 to about 150 microns;
 - a BET surface area, after calcination, in the range of from about 200 to about 260 m²/g;
- 5 and
- a porosity in the range of from about 0.4 to about 1.0 cm³/g.

8. The method of claim 1 wherein said γ -alumina support has been treated, after calcination, with an acidic aqueous solution.

9. The method of claim 8 wherein said acidic aqueous solution has a pH of not more than 5.

10. The method of claim 8 wherein said acidic aqueous solution has a pH of not more than 3.

11. The method of claim 8 wherein said acidic aqueous solution has a pH in the range of from about 3 to about 1.

12. The method of claim 1 wherein said catalyst comprises cobalt supported on said γ -alumina support in a selected amount in the range of from about 10 to about 70 parts by weight (pbw) per 100 pbw of said γ -alumina support.

13. The method of claim 12 wherein said cobalt has been applied to said γ -alumina support by totally aqueous impregnation using an effective composition, and an effective amount, of an aqueous solution to achieve incipient wetness of said γ -alumina support with said selected amount of said cobalt.

14. The method of claim 13 wherein said aqueous solution comprises cobalt nitrate.

15. The method of claim 13 wherein said aqueous solution has a pH of not more than 5.

16. The method of claim 13 wherein said aqueous solution has a pH in the range of from about 3 to about 1.

17. The method of claim 12 wherein said selected amount of said cobalt is in the range of from about 15 pbw to about 55 pbw per 100 pbw of said γ -alumina support.

18. The method of claim 12 wherein said selected amount of said cobalt is in the range of from about 20 pbw to about 45 pbw per 100 pbw of said γ -alumina support.

19. The method of claim 12 wherein said selected amount of said cobalt is about 30% by weight based on the total weight of said catalyst.

20. The method of claim 12 wherein said catalyst is promoted with a selected amount of ruthenium.

21. The method of claim 20 wherein said ruthenium is present in an amount in the range of
5 from about 0.1 to about 8 pbw per 100 pbw of said γ -alumina support.

22. The method of claim 20 wherein said ruthenium is present in an amount in the range of from about 0.2 pbw to about 1.5 pbw per 100 pbw of said γ -alumina support.

23. The method of claim 20 wherein said cobalt and said ruthenium have been applied to said γ -alumina support by totally aqueous coimpregnation using an effective composition, and an effective amount, of an aqueous solution to achieve incipient wetness of said γ -alumina support with said selected amounts of said cobalt and said ruthenium.

24. The method of claim 23 wherein said aqueous solution comprises cobalt nitrate.

25. The method of claim 23 wherein said aqueous solution has a pH of not more than 5.

26. The method of claim 23 wherein said aqueous solution has a pH in the range of from
20 about 3 to about 1.

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27. The method of claim 1 wherein said high agitation reaction system is a three-phase reaction system.

28. The method of claim 1 wherein said high agitation reaction system is a slurry bubble
5 column reactor system.

29. A method for reducing catalyst attrition losses in hydrocarbon synthesis processes conducted in high agitation reaction systems, said method comprising the step of reacting a synthesis gas in a high agitation reaction system in the presence of a catalyst comprising a γ -alumina support which has been treated, after calcination, with an acidic aqueous solution.

30. The method of claim 29 wherein said aqueous solution has a pH of not more than 5.

31. The method of claim 29 wherein said aqueous solution has a pH in the range of from about 3 to about 1.

32. The method of claim 29 wherein said γ -alumina support has been produced from spray-dried, synthetic boehmite.

33. The method of claim 30 wherein said γ -alumina support has:
a substantially spheroidal shape;
an average particle size in the range of from about 10 to about 150 microns;

a BET surface area, after calcination, in the range of from about 200 to about 260 m²/g;

and

a porosity in the range of from about 0.4 to about 1.0 cm³/g.

5 34. The method of claim 29 wherein said catalyst comprises cobalt supported on said γ -alumina support in a selected amount in the range of from about 10 to about 70 pbw per 100 pbw of said γ -alumina support.

35. The method of claim 29 wherein said high agitation reaction system is a three-phase reaction system.

36. The method of claim 29 wherein said high agitation reaction system is a slurry bubble column reactor system.

10 37. A method for reducing catalyst attrition losses in hydrocarbon synthesis processes conducted in high agitation reaction systems, said method comprising the step of reacting a synthesis gas in a high agitation reaction system in the presence of a catalyst comprising cobalt on a γ -alumina support, said cobalt being present on said support in an amount in the range of from about 10 pbw to about 70 pbw per 100 pbw of said γ -alumina support and said cobalt
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20 having been applied to said γ -alumina support by totally aqueous impregnation using an effective composition, and an effective amount, of an aqueous solution to achieve incipient

wetness of said γ -alumina support with said amount of said cobalt, said aqueous solution having a pH of not more than about 5.

38. The method of claim 37 wherein said aqueous solution has a pH in the range of from about 3 to about 1.

39. The method of claim 37 wherein said aqueous solution comprises cobalt nitrate.

40. The method of claim 37 wherein said selected amount of said cobalt is in the range of from about 15 pbw to about 55 pbw per 100 pbw of said γ -alumina support.

41. The method of claim 37 wherein said selected amount of said cobalt is in the range of from about 20 pbw to about 45 pbw per 100 pbw of said γ -alumina support.

42. The method of claim 37 wherein said selected amount of said cobalt is about 30% by weight based on the total weight of said catalyst.

43. The method of claims 37 wherein said catalyst is promoted with a selected amount of ruthenium.

44. The method of claim 43 wherein said ruthenium is present on said support in an amount in the range of from about 0.1 to about 8 pbw per 100 pbw of said γ -alumina support.

45. The method of claim 43 wherein said ruthenium is present on said support in an amount in the range of from about 0.2 pbw to about 1.5 pbw per 100 pbw of said γ -alumina support.

5 46. The method of claim 43 wherein said cobalt and said ruthenium have been applied to said γ -alumina support by totally aqueous coimpregnation using said aqueous solution and wherein said aqueous solution has a composition and is used in an amount effective to achieve incipient wetness of said γ -alumina support with said amount of said cobalt and said selected amount of said ruthenium.

47. The method of claim 46 wherein said aqueous solution comprises cobalt nitrate.

48. The method of claim 37 wherein said γ -alumina support has been produced from spray-dried, synthetic boehmite.

49. The method of claim 48 wherein said γ -alumina support has:
a substantially spheroidal shape;
an average particle size in the range of from about 10 to about 150 microns;
a BET surface area, after calcination, in the range of from about 200 to about 260 m²/g;
20 and
a porosity in the range of from about 0.4 to about 1.0 cm³/g.

50. The method of claim 37 wherein said high agitation reaction system is a three-phase reaction system.

51. The method of claim 37 wherein said high agitation reaction system is a slurry bubble column reactor system.

52. A method for reducing catalyst attrition losses in hydrocarbon synthesis processes conducted in slurry bubble column reactors, said method comprising the step of reacting a synthesis gas in a slurry bubble column reactor in the presence of a catalyst comprising cobalt, on a γ -alumina support, and an amount of a lanthana promoter effective for increasing the attrition resistance of said catalyst in said slurry bubble column reactor.

53. The method of claim 52 wherein:

said cobalt is present in an amount in the range of from about 10 pbw to about 70 pbw per 100 pbw of said γ -alumina support and

said lanthana is present in an amount in the range of from about 0.5 to about 8 pbw per 100 pbw of said γ -alumina support.

54. The method of claim 52 wherein:

said cobalt is present in an amount in the range of from about 15 pbw to about 55 pbw per 100 pbw of said γ -alumina support and

said lanthana is present in an amount in the range of from about 0.5 to about 5.0 pbw
per 100 pbw of said γ -alumina support.

55. The method of claim 54 wherein said lanthana is present in an amount in the range of
5 from about 0.9 pbw to about 2.5 pbw per 100 pbw of said γ -alumina support.

56. A method of producing an attrition resistant catalyst having a calcined γ -alumina
support, said method comprising the step, after calcination of but before adding catalytic
material to said support, of treating said support with an acidic aqueous solution having an
acidity level effective for increasing the attrition resistance of said catalyst.

57. The method of claim 56 wherein said acidic aqueous solution comprises water and nitric
acid.

58. The method of claim 56 wherein said acidic aqueous solution has a pH of not more than
5.

59. The method of claim 56 wherein said acidic aqueous solution has a pH in the range of
from about 3 to about 1.

60. The method of claim 56 wherein said γ -alumina support has been produced from spray-
dried, synthetic boehmite.

61. A method of producing an attrition resistant catalyst support, said method comprising the step of treating calcined γ -alumina with an acidic aqueous solution having an acidity level effective for increasing the attrition resistance of said calcined γ -alumina.

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62. The method of claim 61 wherein said acidic aqueous solution comprises water and nitric acid.

63. The method of claim 61 wherein said acidic aqueous solution consists essentially of water and at least one acid.

64. The method of claim 63 wherein said acid is nitric acid.

65. The method of claim 61 wherein said acidic aqueous solution has a pH of not more than 5.

66. The method of claim 61 wherein said acidic aqueous solution has a pH in the range of from about 3 to about 1.

20 67. A catalyst having improved attrition resistance, said catalyst comprising a calcined γ -alumina support and said catalyst having been produced by a method comprising the step, after calcination of but before adding catalytic materials to said support, of treating said support with

an acidic aqueous solution having an acidity level effective for increasing the attrition resistance of said catalyst.

68. The catalyst of claim 67 wherein said acidic aqueous solution comprises water and nitric acid.

69. The catalyst of claim 67 wherein said acidic aqueous solution has a pH of not more than 5.

70. The catalyst of claim 67 wherein said acidic aqueous solution has a pH in the range of from about 3 to about 1.

71. A catalyst support having improved attrition resistance, said catalyst support being produced by a method comprising the step of treating calcined γ -alumina with an acidic aqueous solution having an acidity level effective for increasing the attrition resistance of said calcined γ -alumina.

72. The catalyst support of claim 71 wherein said acidic aqueous solution comprises water and nitric acid.

73. The catalyst support of claim 71 wherein said acidic aqueous solution consists essentially of water and at least one acid.

74. The catalyst support of claim 73 wherein said acid is nitric acid.

75. The catalyst support of claim 71 wherein said acidic aqueous solution has a pH of not
5 more than 5.

76. The catalyst support of claim 71 wherein said acidic aqueous solution has a pH in the
range of from about 3 to about 1.

77. A method of reducing catalyst attrition losses in hydrocarbon synthesis processes
conducted in high agitation reaction systems, said method comprising the step of reacting a
synthesis gas in a high agitation reaction system in the presence of a catalyst comprising a γ -
alumina support, wherein said γ -alumina support is produced from boehmite having a
crystallite size, in the 021 plane, in the range of from about 30 to about 55 Ångstroms.

78. The method of claim 77 wherein said crystallite size, in the 021 plane, is in the range of
from about 40 to about 50 Ångstroms.

79. The method of claim 77 wherein said γ -alumina support includes an amount of titanium
20 of at least 800 ppm by weight.

80. The method of claim 77 wherein said γ -alumina support has:
a substantially spheroidal shape;
an average particle size in the range of from about 10 to about 150 microns;
a BET surface area, after calcination, in the range of from about 200 to about 260 m²/g;

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and

a porosity in the range of from about 0.4 to about 1.0 cm³/g.

81. The method of claim 77 wherein said catalyst comprises cobalt supported on said γ -alumina support in a selected amount in the range of from about 10 to about 70 parts by weight (pbw) per 100 pbw of said γ -alumina support.

82. The method of claim 81 wherein said cobalt has been applied to said γ -alumina support by totally aqueous impregnation using an effective composition, and an effective amount, of an aqueous solution to achieve incipient wetness of said γ -alumina support with said selected amount of said cobalt.

83. The method of claim 82 where said aqueous solution has a pH in the range of from about 3 to about 1.

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84. The method of claim 77 wherein said high agitation reaction system is a three-phase reaction system.

85. The method of claim 77 wherein said high agitation reaction system is a slurry bubble column reaction system.

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